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Quantitative Passive Diffusive Sampling for Assessing Soil Vapor Intrusion to Indoor Air

Todd McAlary and Hester Groenevelt, Geosyntec Consultants, Inc.,
T. Gorecki and Suresh Seethapathy, University of Waterloo,
D. Crump, Cranfield University,
P. Sacco, Fondazione Salvatore Maugeri,
H. Hayes, Air Toxics Limited,
M. Tuday, Columbia Analytical Services,
B. Schumacher, USEPA,
P. Johnson, Arizona State University

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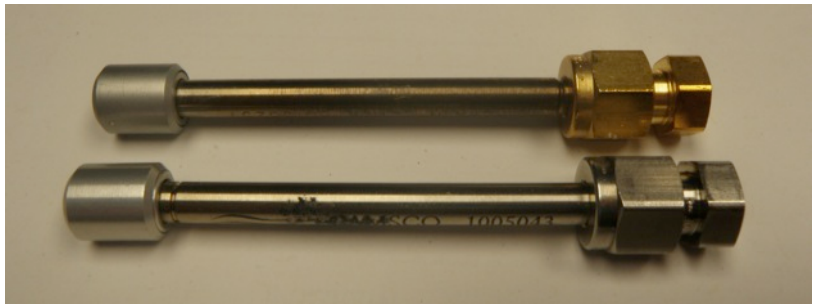
Passive Samplers



ATD Tubes

3M OVM 3500

The mass (M) and time (t) are measured accurately. Key is to know the uptake rate (UR)

$$C_0 = \frac{M}{UR\ t}$$

Waterloo Membrane Sampler™

Radiello™

Differences: size, uptake rates, sorbents, medium of uptake, method of analysis

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Benefits of Passive Sampling

- Simple (minimal training, less risk of leaks)
- Time-weighted average concentration
  (up to a week or a month if needed)
- Low reporting limits with no premium cost
- Smaller – easy to ship, discrete to deploy
- Long history of use in Industrial Hygiene
- Less expensive
- Other benefits unique to each sampler

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Laboratory Test Compound List

Analyte	Koc (mL/g)	OSWER indoor conc. at 10^{-6} risk (ppb)	Vapour pressure (atm)	Water solubility (g/l)
1,1,1-Trichloroethane	**110**	400	0.16	1.33
1,2,4-Trimethylbenzene	**472**	1.2	0.00197	0.0708
1,2-Dichloroethane	**174**	0.023	0.107	8.52
2-Butanone (MEK)	**134**	340	0.1026	~ 256
Benzene	**59**	0.10	0.125	1.75
Carbon tetrachloride	**174**	0.026	0.148	0.793
Naphthalene	**2,000**	0.57	0.000117	0.031
n-Hexane	**3,000**	57	0.197	0.0128
Tetrachloroethene	**155**	0.12	0.0242	0.2
Trichloroethene	**166**	0.22	0.0948	1.1

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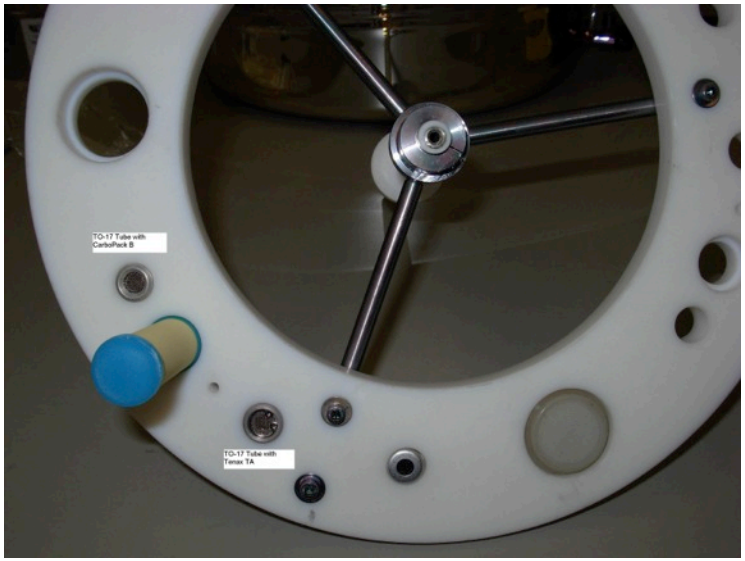
Experimental Apparatus



24 chambers x
5 sampler types x
3 replicates x
10 chemicals
= 3600 measurements


HEMCO

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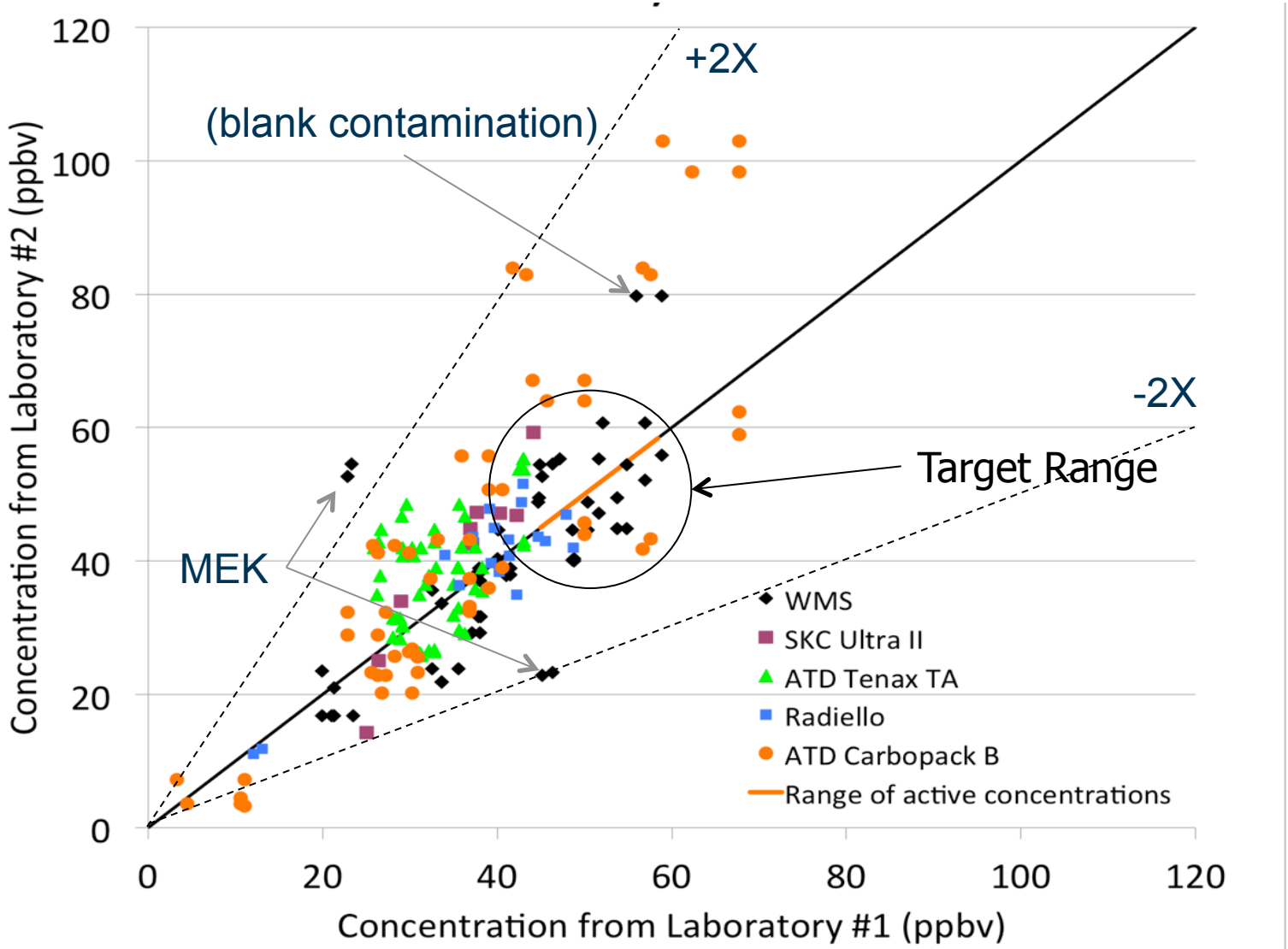
Interlab Test – Youden Plot



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Fractional Factorial Testing

Run #	Approximate Concentration (ppbv)	Approximate Temperature (°C)	Face Velocity (m/s)	Duration (days)	Approximate Humidity (%R.H.)
1	100	17	0.41	1	90
2	1	17	0.014	1	90
3	100	30	0.41	1	30
4	1	30	0.014	1	30
5	100	30	0.41	7	90
6	1	30	0.014	7	90
7	100	17	0.41	7	30
8	1	17	0.014	7	30
9	50	20	0.23	4	60
10	50	20	0.23	4	60
11	100	17	0.014	1	30
12	1	17	0.41	1	30
13	100	17	0.014	7	90
14	1	17	0.41	7	90
15	100	30	0.014	7	30
16	1	30	0.41	7	30
17	100	30	0.014	1	90
18	1	30	0.41	1	90

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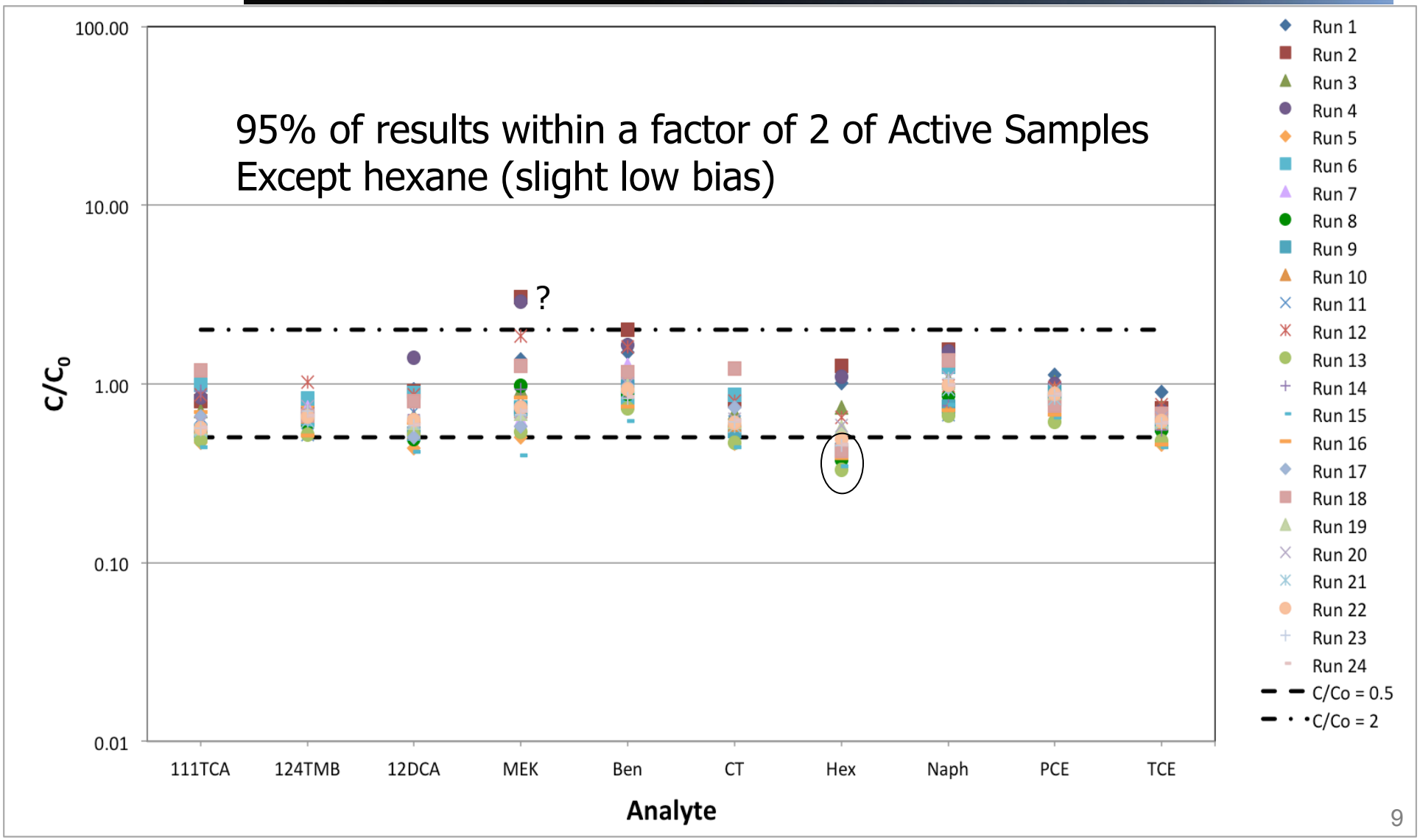
ATD Tenax TA



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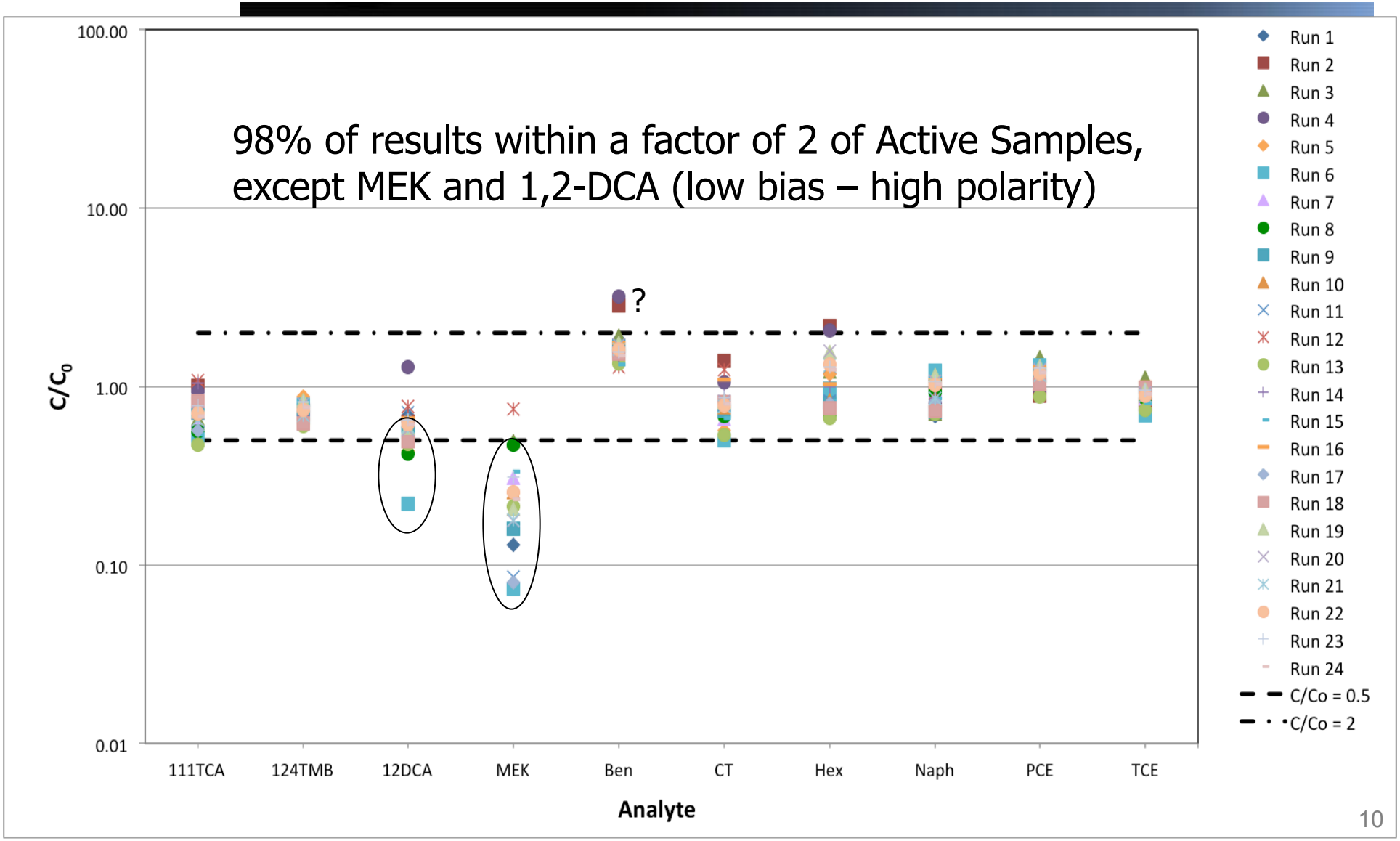
ATD Carbopack B



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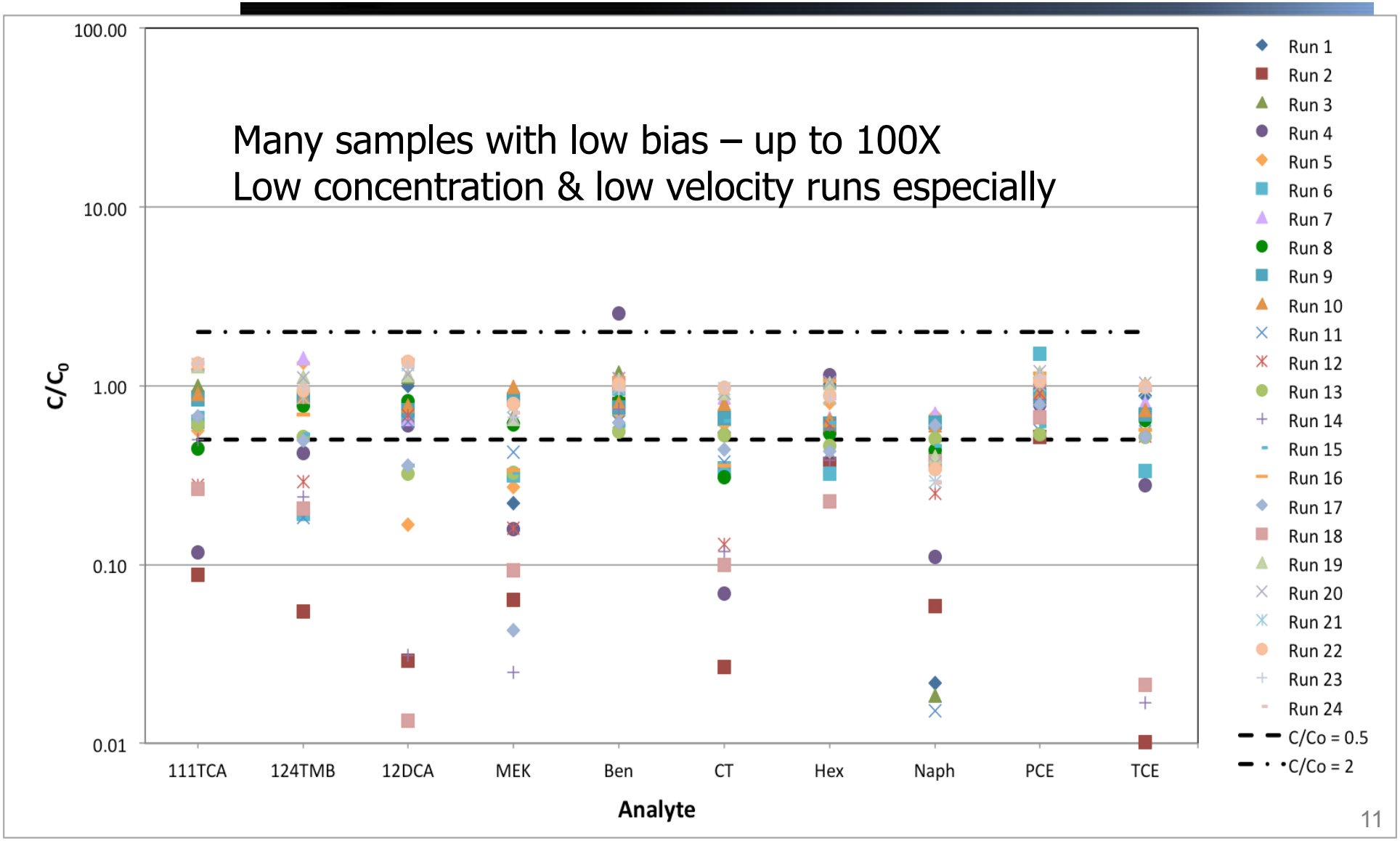
SKC Ultra



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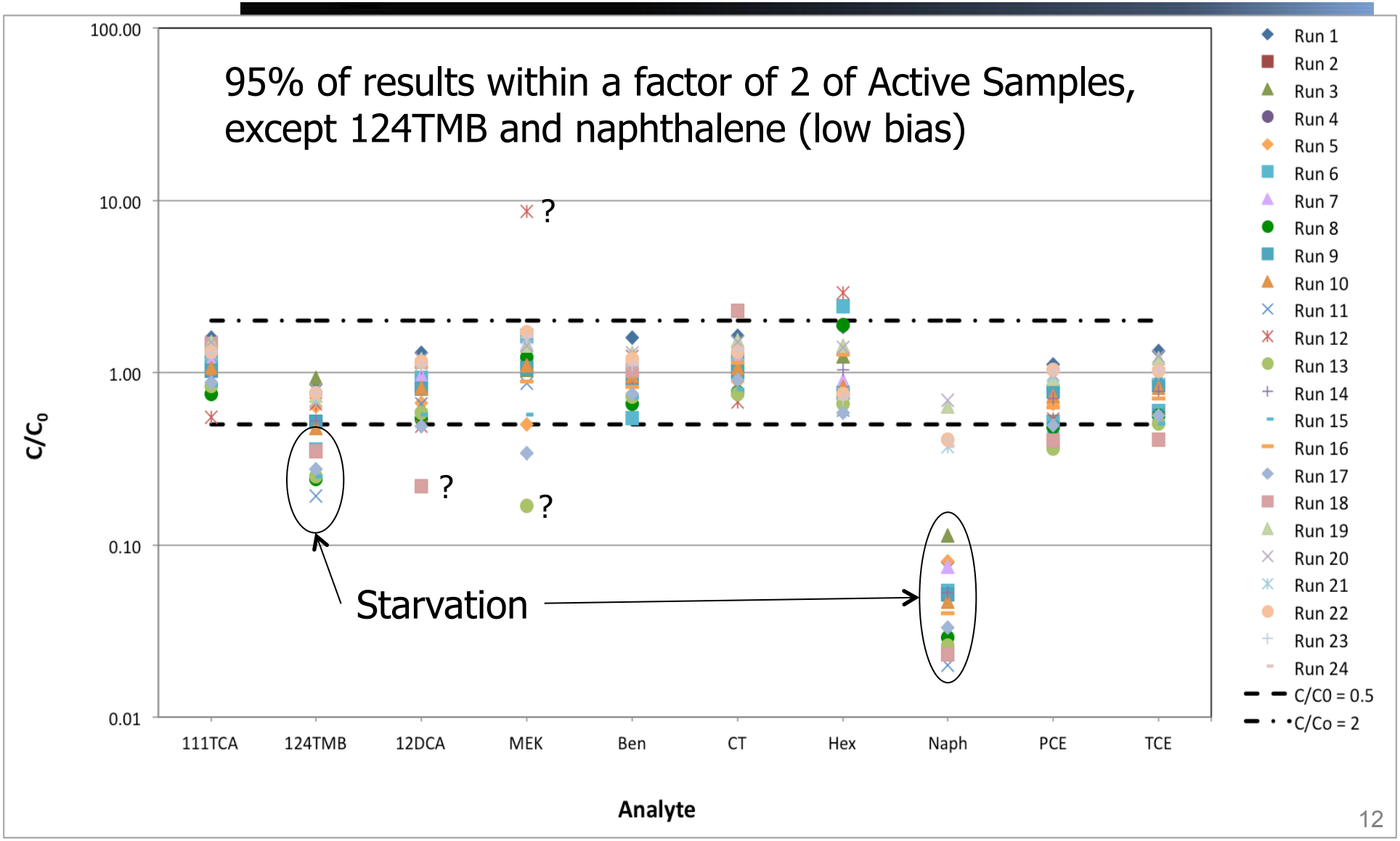
Waterloo Membrane Sampler



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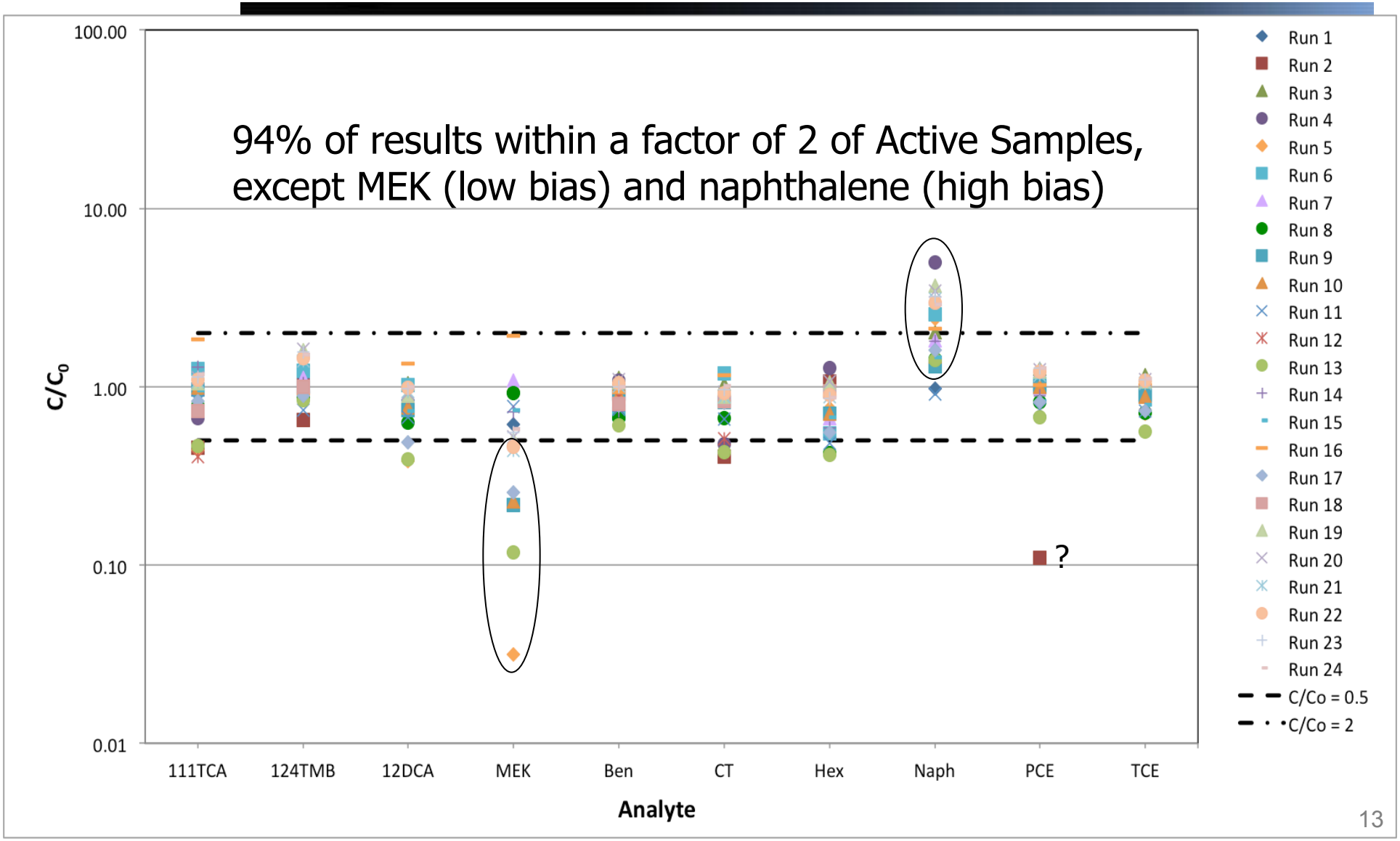
Radiello



ANOVA Analysis

Table 1: Statistical Significance of the Main Factors in the Fractional Factorial Experiments

Sampler Type	Analyte	Relative Humidity	Temperature	Face Velocity	Exposure Time	Concentration
ATD Carbopack	1,1,1-Trichloroethane	0.0778	0.0281	0.0106	0.0003	<.0001
ATD Carbopack	1,2,4-Trimethylbenzene	0.3181	0.0009	0.1245	0.5664	0.0011
ATD Carbopack	1,2-Dichloroethane	0.0012	0.6819	0.7406	<.0001	0.1371
ATD Carbopack	2-Butanone (MEK)	0.0693	0.4097	0.0603	0.7378	0.0119
ATD Carbopack	Hexane	0.7999	0.2913	0.4002	0.0272	0.1177
ATD Carbopack	Benzene	0.4718	0.2468	0.0547	0.0023	0.0331
ATD Carbopack	Carbon tetrachloride	0.0434	0.2975	0.3501	<.0001	<.0001
ATD Carbopack	Naphthalene	0.2629	0.6088	0.293	0.007	0.0778
ATD Carbopack	Trichloroethene	0.0113	0.2781	0.0002	<.0001	0.9484
ATD Carbopack	Tetrachloroethene	0.8513	0.004	0.0071	0.8484	0.0727
ATD Tenax	1,1,1-Trichloroethane	<.0001	0.2715	0.0021	<.0001	<.0001
ATD Tenax	1,2,4-Trimethylbenzene	0.9169	0.8868	0.0121	0.0296	0.2864
ATD Tenax	1,2-Dichloroethane	0.9154	0.8908	0.4733	<.0001	<.0001
ATD Tenax	2-Butanone (MEK)	0.7719	0.0799	0.1479	<.0001	<.0001
ATD Tenax	Hexane	0.6362	0.21	0.6114	<.0001	0.1148
ATD Tenax	Benzene	0.8106	0.0059	0.438	<.0001	0.0442
ATD Tenax	Carbon tetrachloride	<.0001	0.0229	0.0159	<.0001	<.0001
ATD Tenax	Naphthalene	0.311	0.2147	0.565	0.025	0.0347
ATD Tenax	Trichloroethene	0.5875	0.0002	0.0153	<.0001	0.475
ATD Tenax	Tetrachloroethene	0.3221	0.4522	0.11	<.0001	0.9827
RADIELLO	1,1,1-Trichloroethane	0.1005	0.0261	0.003	0.0899	0.0548
RADIELLO	1,2,4-Trimethylbenzene	0.6688	0.0007	<.0001	0.1133	0.0451
RADIELLO	1,2-Dichloroethane	0.0005	0.054	0.0002	0.0327	<.0001
RADIELLO	2-Butanone (MEK)	<.0001	0.5801	0.0003	0.0738	<.0001
RADIELLO	Hexane	0.1795	0.0066	0.0021	<.0001	0.0035
RADIELLO	Benzene	0.0047	0.0496	0.0012	<.0001	0.6113
RADIELLO	Carbon tetrachloride	0.4994	0.0143	0.0513	0.1724	0.9018
RADIELLO	Naphthalene	0.6635	0.0008	0.933	0.1183	0.0005
RADIELLO	Trichloroethene	0.001	0.0032	<.0001	0.0002	0.0169
RADIELLO	Tetrachloroethene	0.2158	0.0023	<.0001	0.3477	0.9109
SKC	1,1,1-Trichloroethane	0.0906	0.1691	0.0055	0.0096	0.0001
SKC	1,2,4-Trimethylbenzene	0.1362	0.3054	0.0012	0.0004	<.0001
SKC	1,2-Dichloroethane	<.0001	0.5187	0.1033	0.9879	0.6424
SKC	2-Butanone (MEK)	<.0001	0.2819	0.3914	0.0073	0.0028
SKC	Hexane	0.0006	0.0398	0.012	0.4921	0.1584
SKC	Benzene	0.0318	0.0551	0.9085	0.0218	0.0125
SKC	Carbon tetrachloride	0.0223	0.2682	0.032	<.0001	<.0001
SKC	Naphthalene	0.1182	0.1437	0.6579	<.0001	0.1122
SKC	Trichloroethene	<.0001	0.9977	0.0306	0.5618	<.0001
SKC	Tetrachloroethene	0.4868	0.0368	0.018	0.0097	0.1261
WMS	1,1,1-Trichloroethane	0.0224	0.9489	0.0042	0.6355	0.4719
WMS	1,2,4-Trimethylbenzene	0.7716	0.7992	<.0001	0.1467	0.0194
WMS	1,2-Dichloroethane	0.7347	0.1749	0.0054	0.0325	0.1887
WMS	2-Butanone (MEK)	0.5881	0.3369	0.14	0.0319	0.0027
WMS	Hexane	0.6198	0.4942	0.022	0.0003	0.0001
WMS	Benzene	0.5712	0.9017	0.0328	0.0012	0.0099
WMS	Carbon tetrachloride	0.0016	0.3838	0.0035	0.0766	0.0553
WMS	Naphthalene	0.9025	0.4298	<.0001	0.5432	0.006
WMS	Trichloroethene	0.6289	0.0325	0.0006	0.8376	0.0124
WMS	Tetrachloroethene	0.5923	0.1477	<.0001	0.9894	0.0074

red highlighted cells indicate statistical significance when alpha=0.05, therefore, p-value<0.05 = significant

Highlighted cells are statistically significant at the 5% level.

Need to think about whether "statistically significant" is also "practically significant"

95% within 2X is actually pretty good

If only we could predict the challenging compounds

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Field Testing of Indoor Air

Navy San Diego, CA
Cherry Point, NC
CRREL, NH

3 locations/site
5 passive samplers
Summa cans
Triplicates of each

Thanks to Ignacio Rivera of SPAWAR, Jason Williams of Cherry Point and Louise Parker of CRREL

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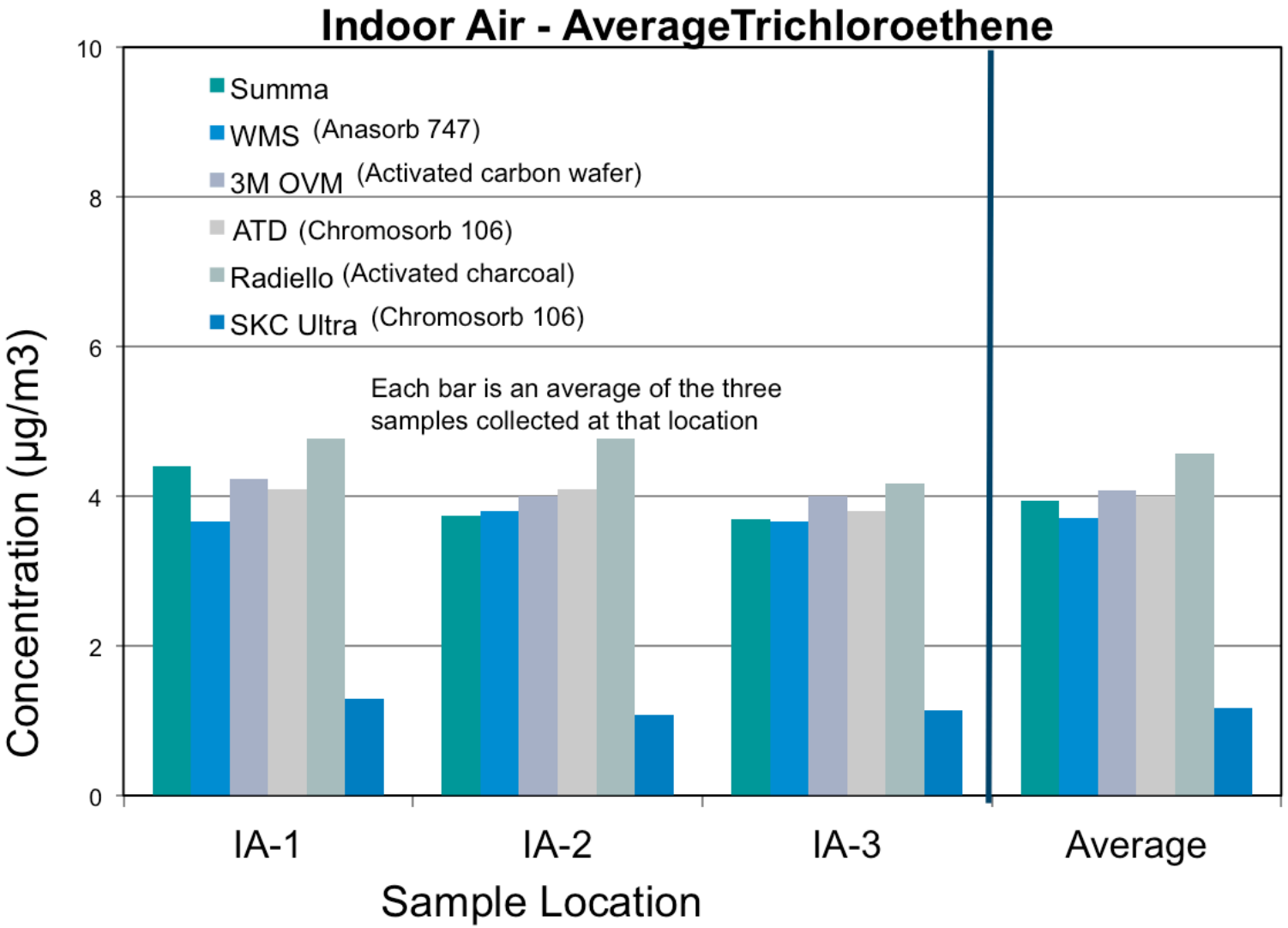
Indoor Air TCE at San Diego



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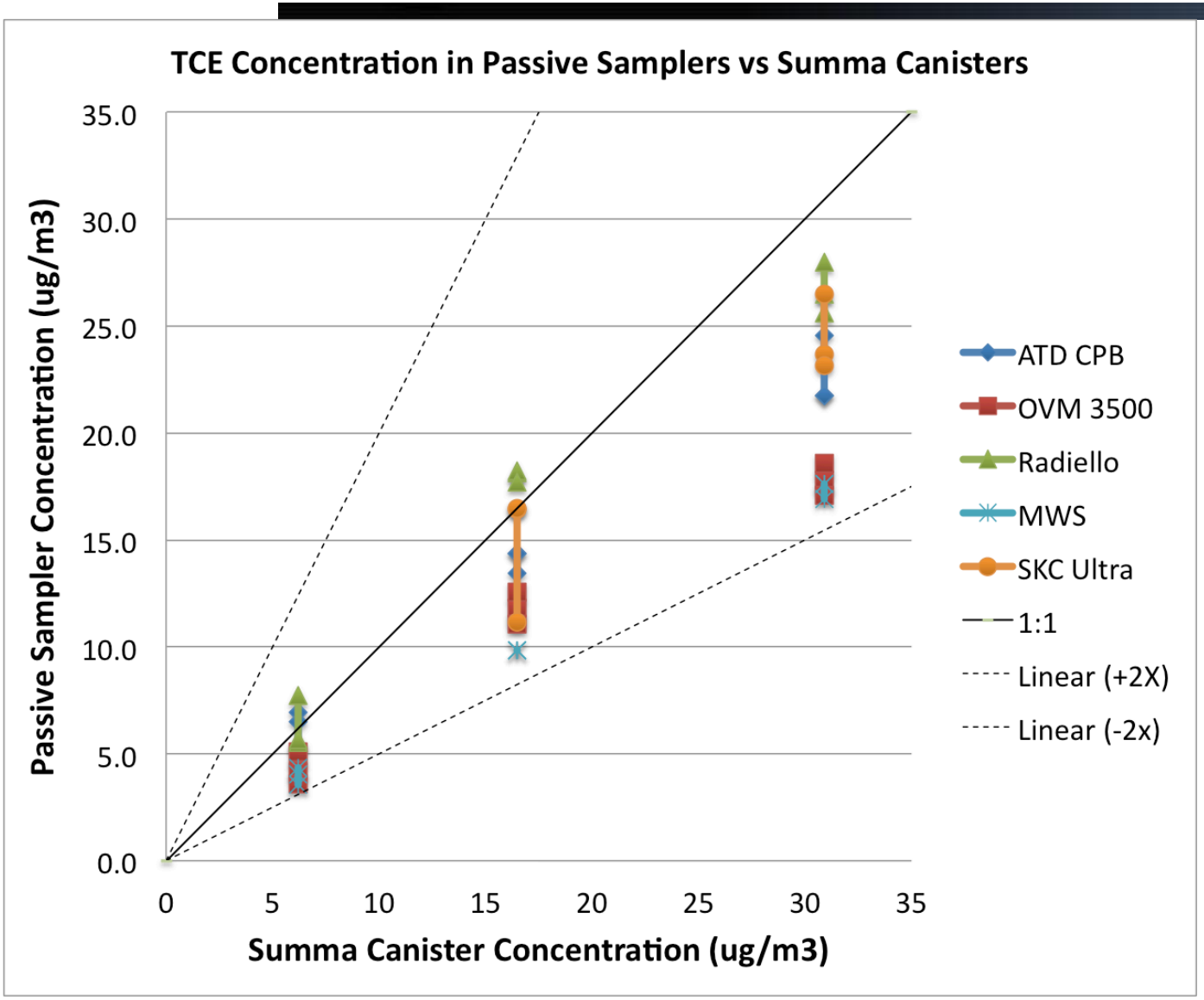
Indoor Air at CRREL



All passive sampler results were within 2X of Summa canister data for TCE

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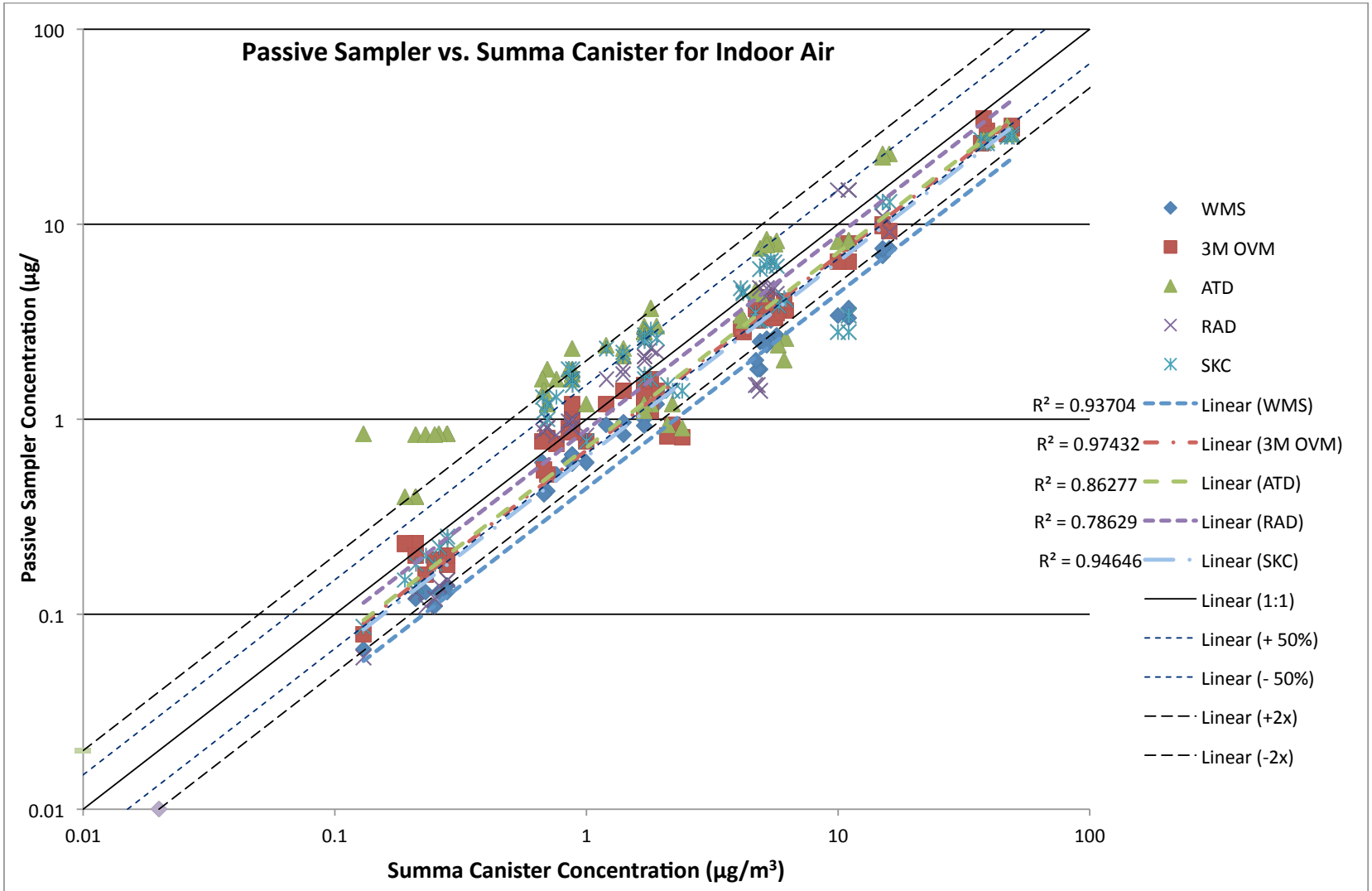
Indoor Air VOCs at Cherry Point



Broader range (>100X), but still almost all passive data are within 2X of Summa canisters

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High Concentration Lab Tests

(To mimic soil gas conditions)

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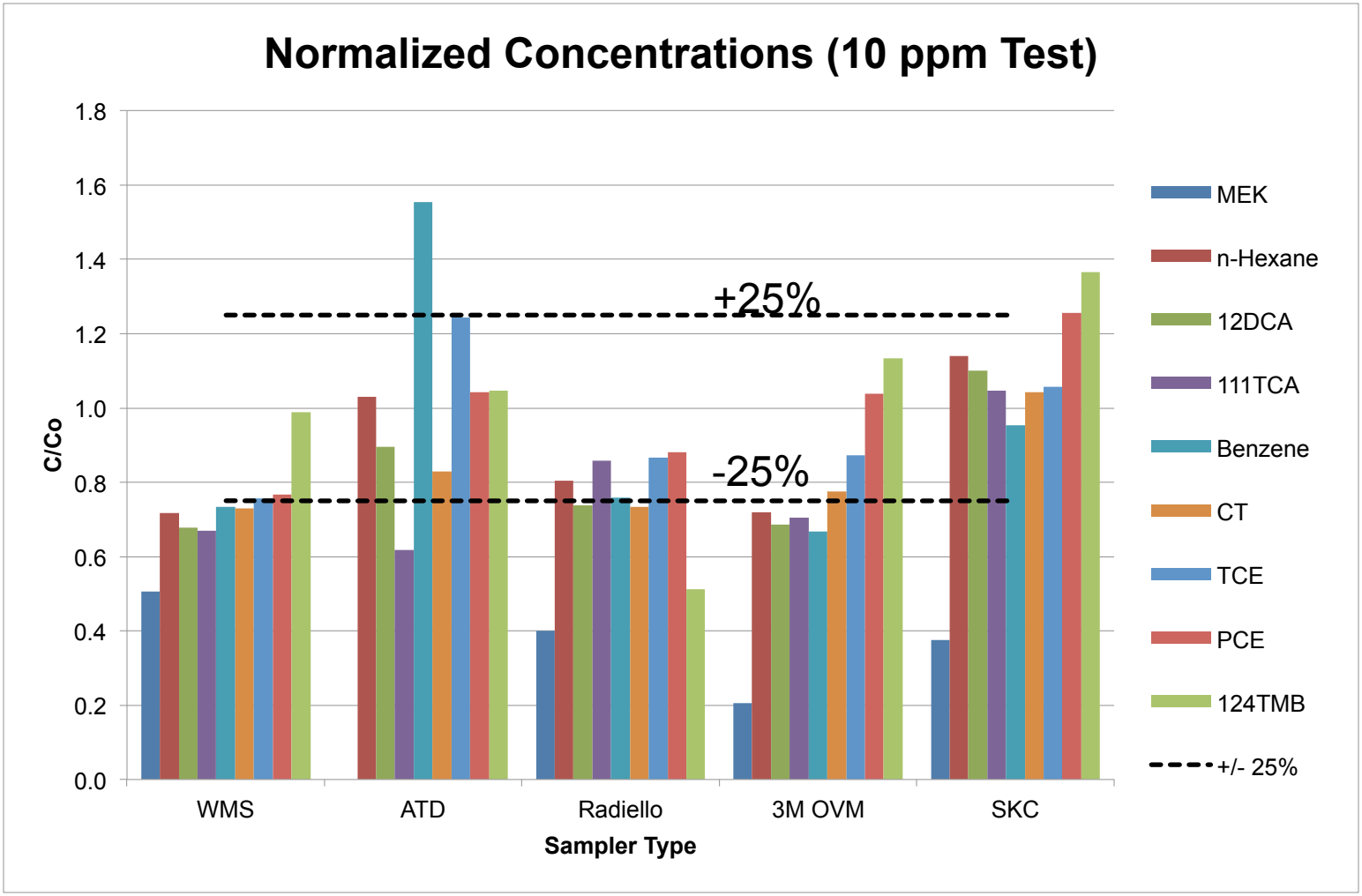
High Concentration Lab Tests

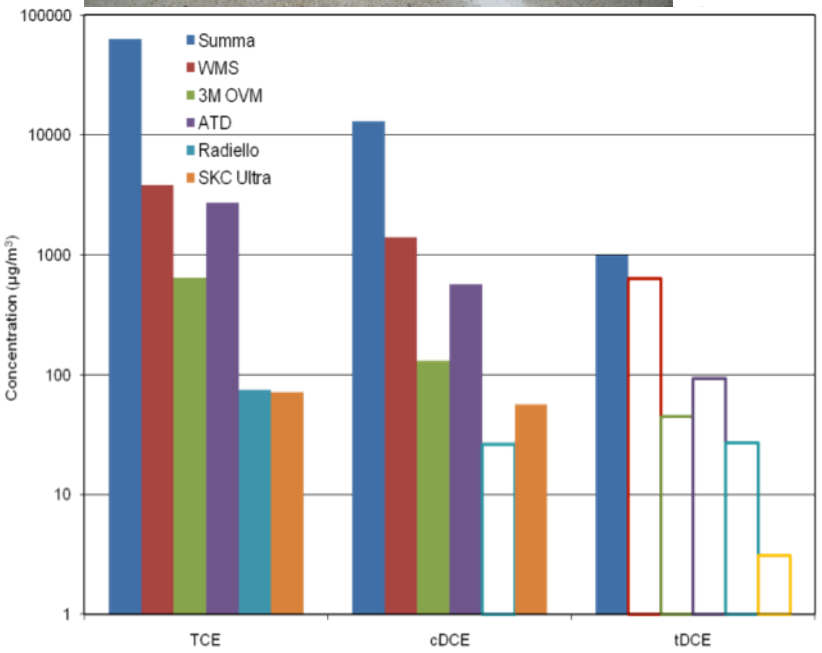
High Concentrations Test Results

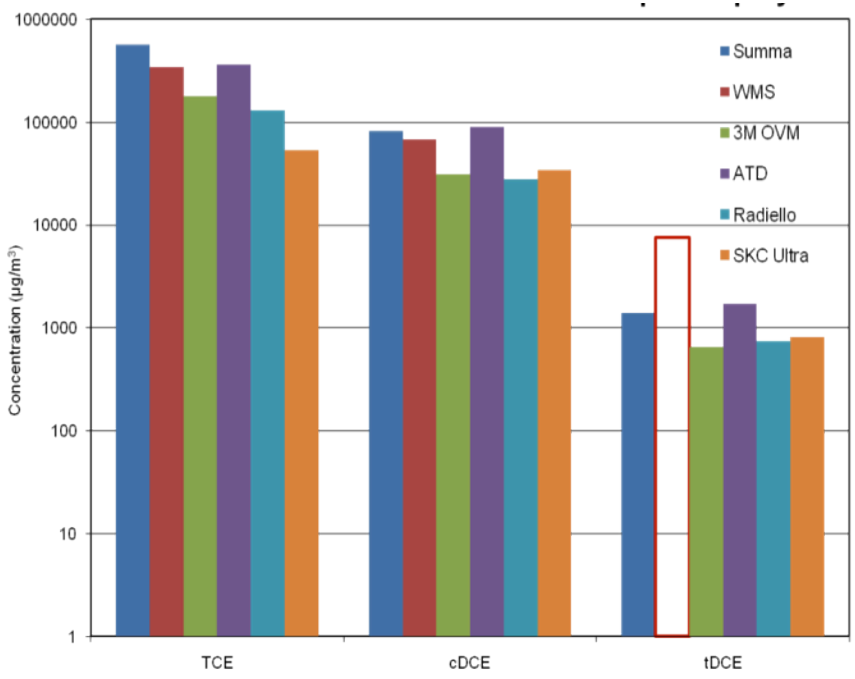


Sub-Slab – Navy San Diego

Sub-slab samples only
Fully-passive and with PID purging (flow-through)

Starvation proportional to uptake rate
Less starvation for semi-passive samples





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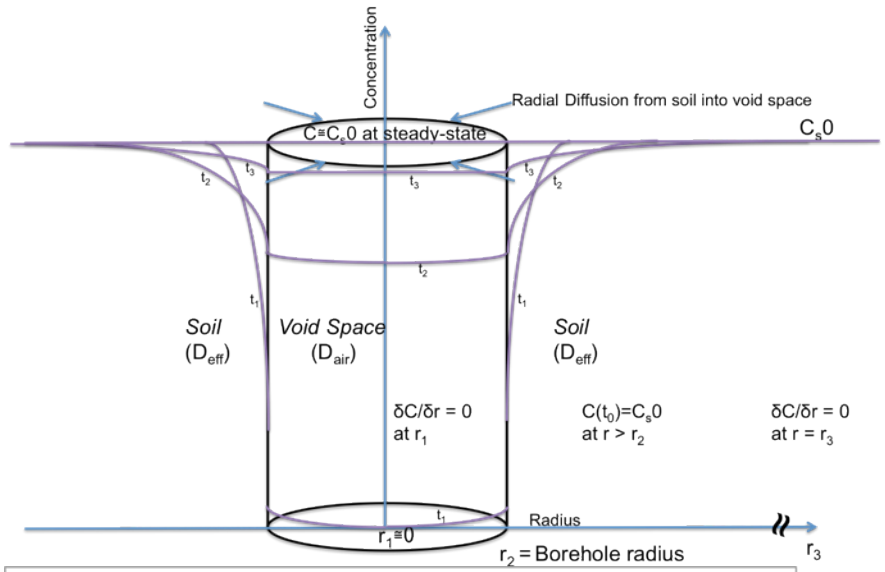
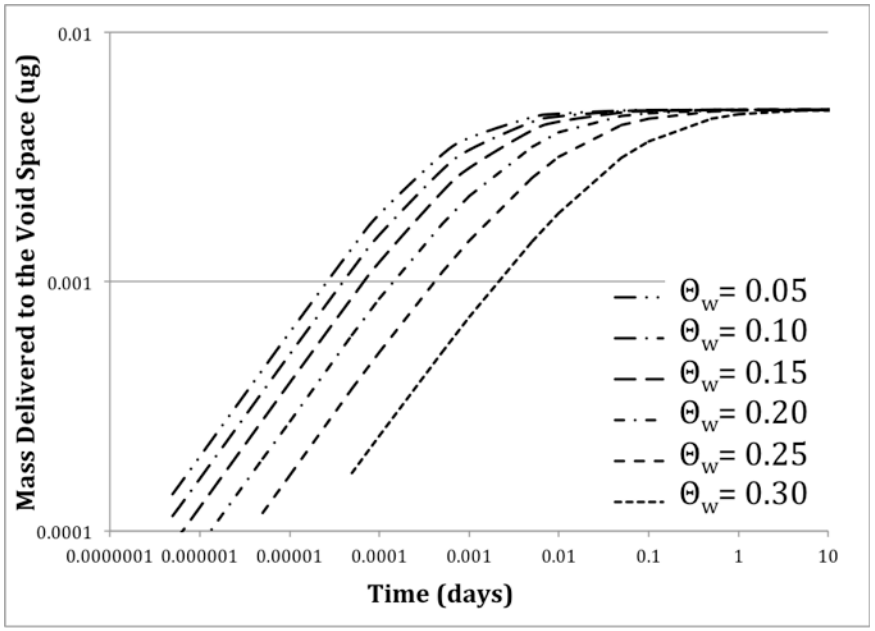
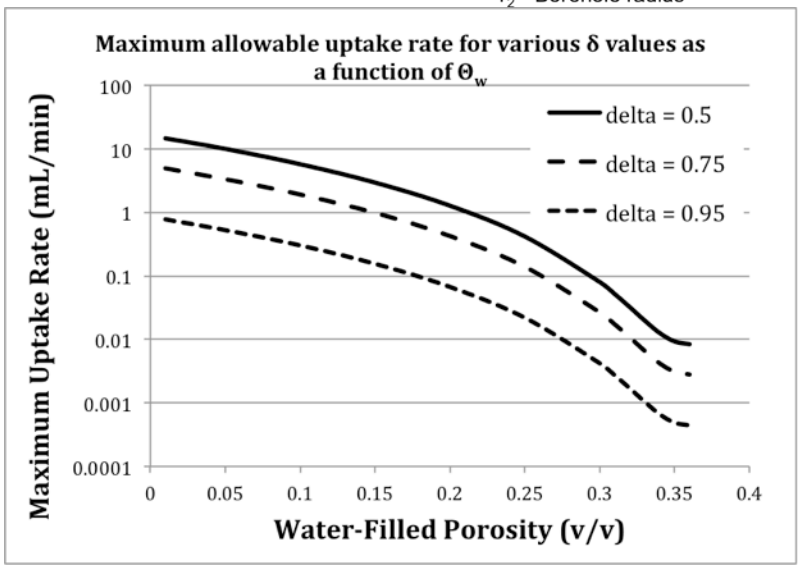
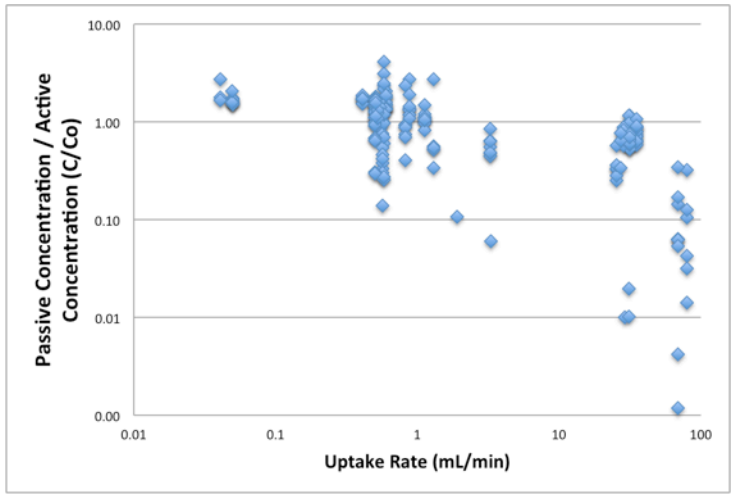
Transient and Steady-State Modeling









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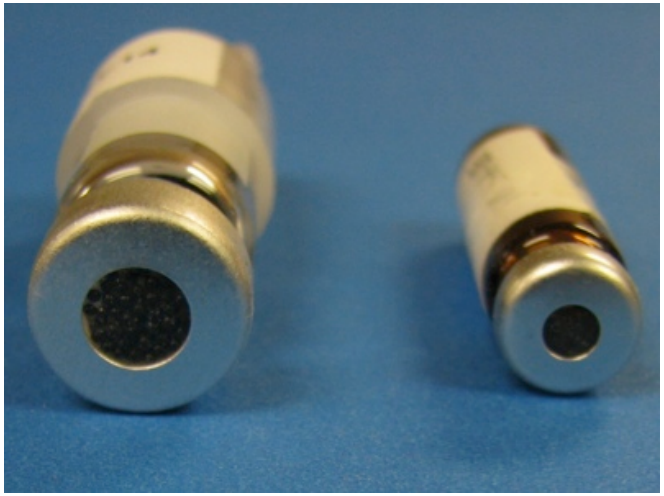
Modified Uptake Rates

Lower uptake rate = less starvation

SKC Ultra II and 12-hole Cap

ATD Tube & Pinhole Cap



WMS and Low-Uptake WMS

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Sorbent Selection

Carbopack B

(Graphitized Carbon Black)
Surface Area: 100 m^2/g
Desorption Temperature: 330 °C

Challenge Volume (Liters)

	0.2	1	5	10	20	100
Halocarbon 12						
Chloromethane						
Halocarbon 114						
Vinyl chloride						
1,3-Butadiene						
Bromomethane						
Chloroethane						
Halocarbon 11						
Acrylonitrile						
1,1-Dichloroethene						
Methylene chloride						
3-Chloropropene						
Halocarbon 113						
1,1-Dichloroethane						
cis-1,2-Dichloroethene						
Chloroform						
1,2-Dichloroethane						
1,1,1-Trichloroethane						
Benzene						
Carbon tetrachloride						
1,2-Dichloropropane						
Trichloroethene						
cis-1,3-Dichloropropene						
trans-1,3-Dichloropropene						
1,1,2-Trichloroethane						
Toluene						
1,2-Dibromoethane						
Tetrachloroethene						
Chlorobenzene						
Ethylbenzene						
m & p-Xylene						
Styrene						
1,1,2,2-Tetrachlorethane						
o-Xylene						
4-Ethyltoluene						
1,3,5-Trimethylbenzene						
1,2,4-Trimethylbenzene						
1,3-Dichlorobenzene						
1,4-Dichlorobenzene						
1,2-Dichlorobenzene						
1,2,4-Trichlorobenzene						
Hexachlorobutadiene						

Performance Key
Safe to use: Recovery is greater than 80%
Caution: Recovery is between 21 to 79%
Not Recommended: Recovery is less than 20%
* indicates this analyte was strongly adsorbed

SUPELCO

Carbopack X

(Graphitized Carbon Black)
Surface Area: 240 m^2/g
Desorption Temperature: 330 °C

Challenge Volume (Liters)

	0.2	1	5	10	20	100
Halocarbon 12						
Chloromethane						
Halocarbon 114						
Vinyl chloride						
1,3-Butadiene						
Bromomethane						
Chloroethane						
Halocarbon 11						
Acrylonitrile						
1,1-Dichloroethene						
Methylene chloride						
3-Chloropropene						
Halocarbon 113						
1,1-Dichloroethane						
cis-1,2-Dichloroethene						
Chloroform						
1,2-Dichloroethane						
1,1,1-Trichloroethane						
Benzene						
Carbon tetrachloride						
1,2-Dichloropropane						
Trichloroethene						
cis-1,3-Dichloropropene						
trans-1,3-Dichloropropene						
1,1,2-Trichloroethane						
Toluene						
1,2-Dibromoethane						
Tetrachloroethene						
Chlorobenzene						
Ethylbenzene						
m & p-Xylene						
Styrene						
1,1,2,2-Tetrachlorethane						
o-Xylene						
4-Ethyltoluene *						
1,3,5-Trimethylbenzene *						
1,2,4-Trimethylbenzene *						
1,3-Dichlorobenzene *						
1,4-Dichlorobenzene *						
1,2-Dichlorobenzene *						
1,2,4-Trichlorobenzene *						
Hexachlorobutadiene						

Performance Key
Safe to use: Recovery is greater than 80%
Caution: Recovery is between 21 to 79%
Not Recommended: Recovery is less than 20%
* indicates this analyte was strongly adsorbed

SUPELCO

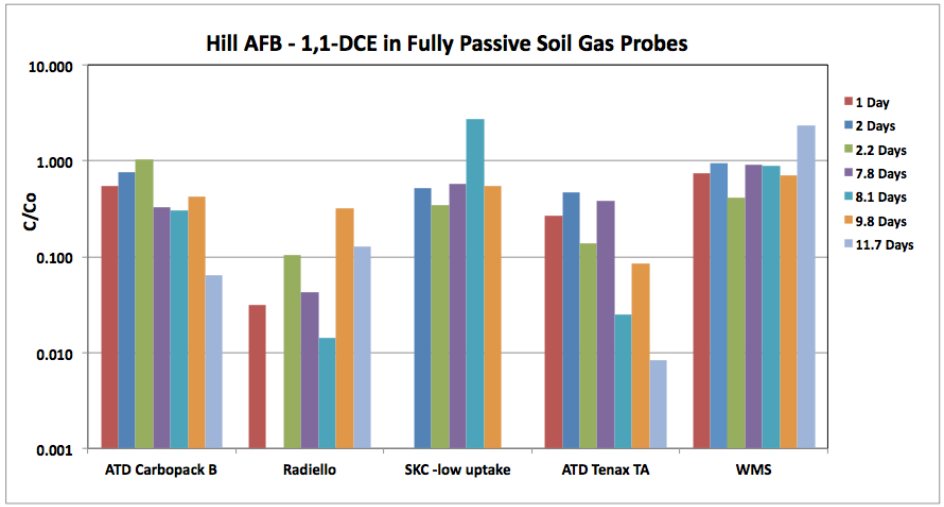
Soil Gas @ 12 ft – Hill AFB

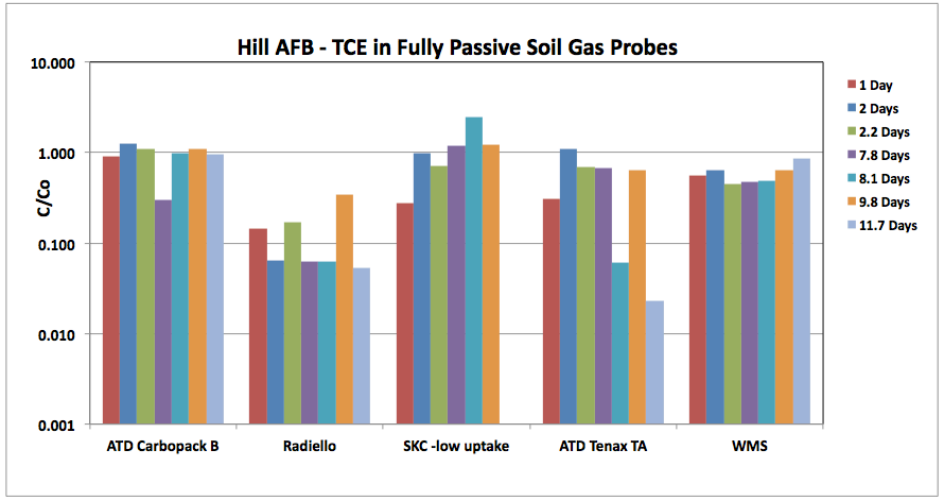
6 probes -12 ft deep

Latin Square Design

1 to 12 day exposures

C_o Measured using combination of Summa and Hapsite GC/MS





Negative bias for long duration with ATD-Tenax
Negative bias for high uptake rate (Radiello)
Otherwise, encouraging results for TCE and DCE

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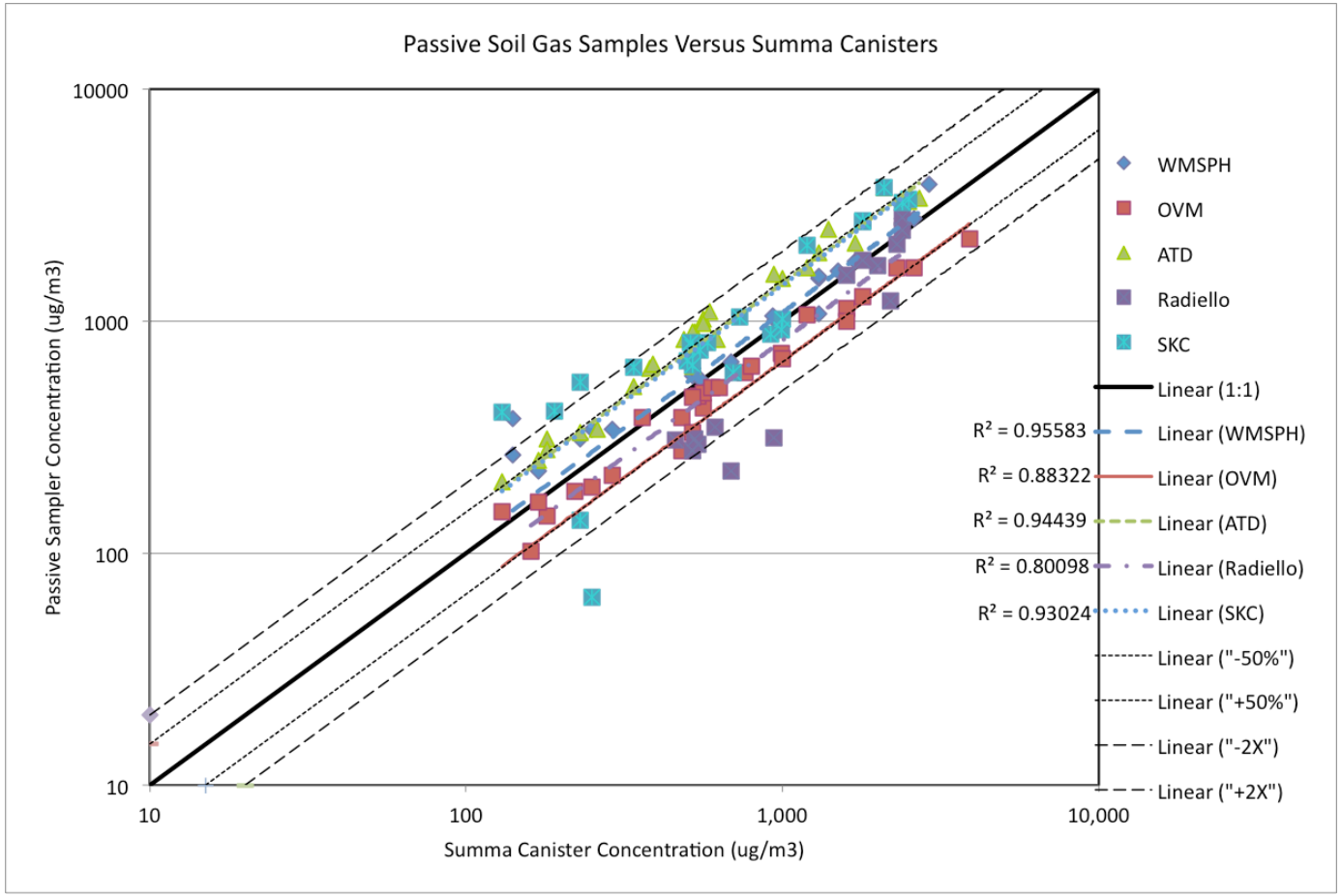
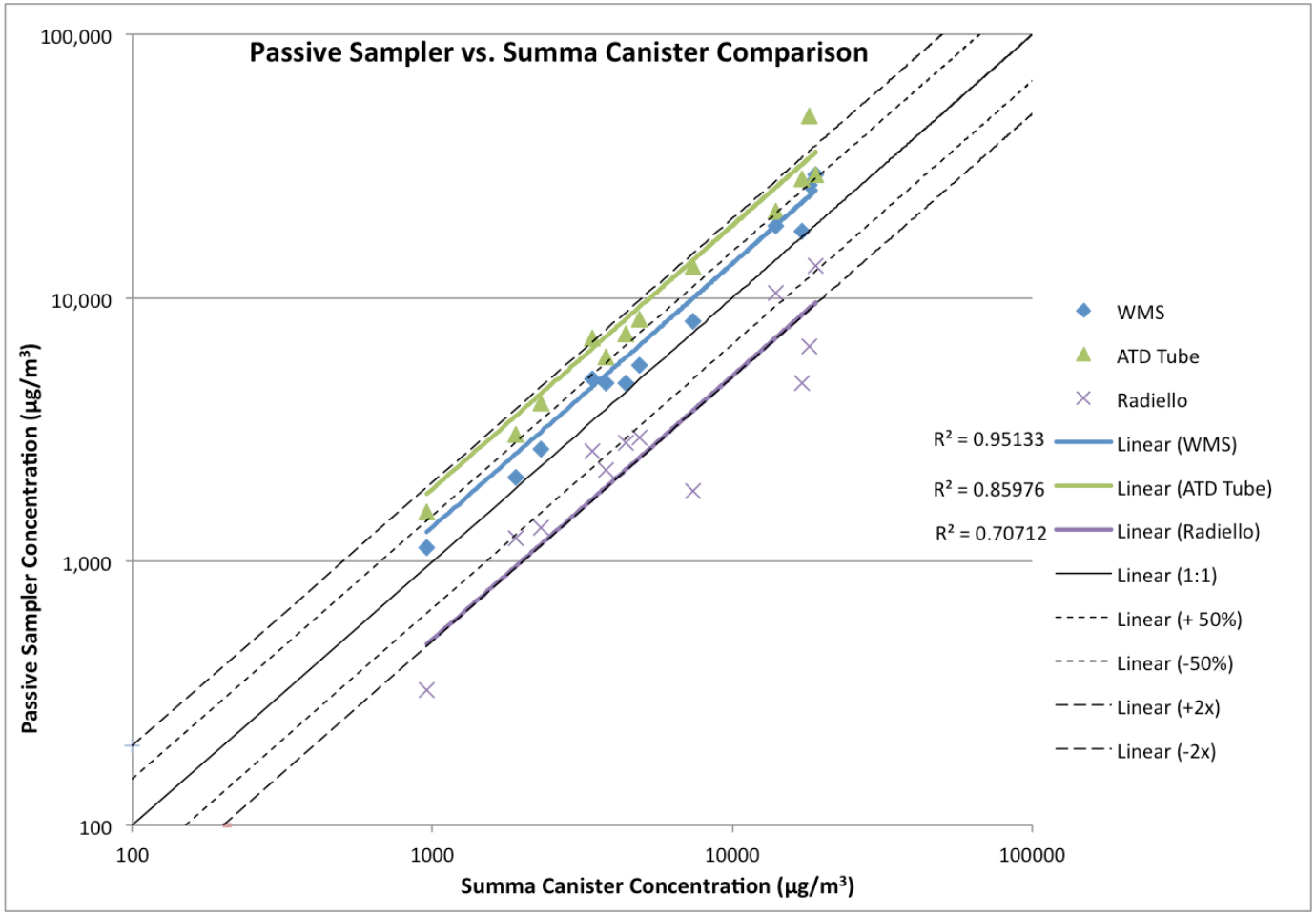
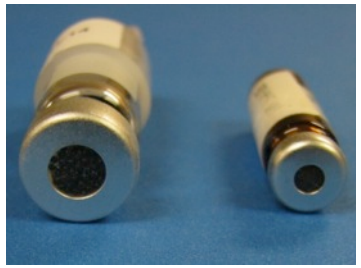
Soil Vapor Sampling – NAS JAX



Probes to 3-4 feet deep, exposure durations of 20, 40 and 60 minutes
Strong correlations, regression slopes all near 1.0

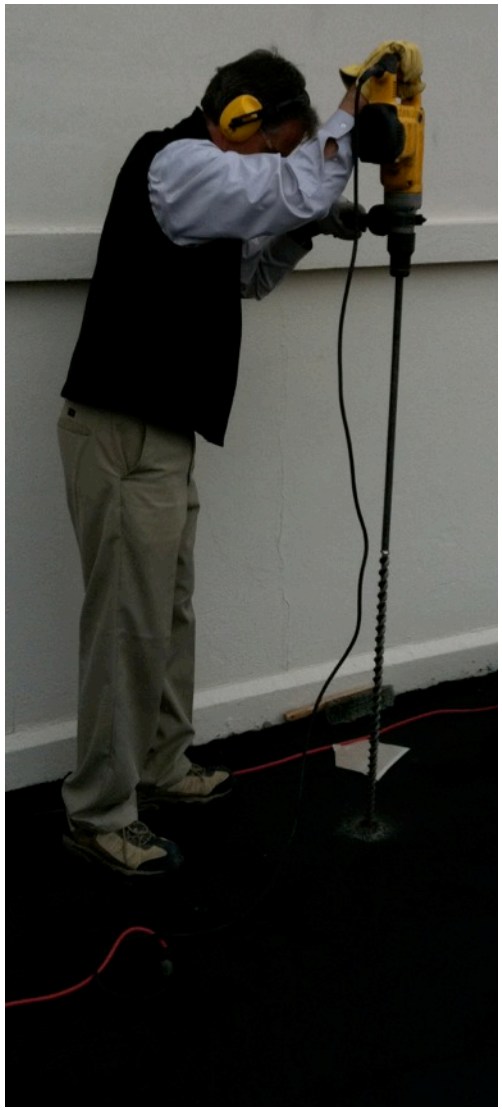
Passive Sub-Slab – NAS JAX

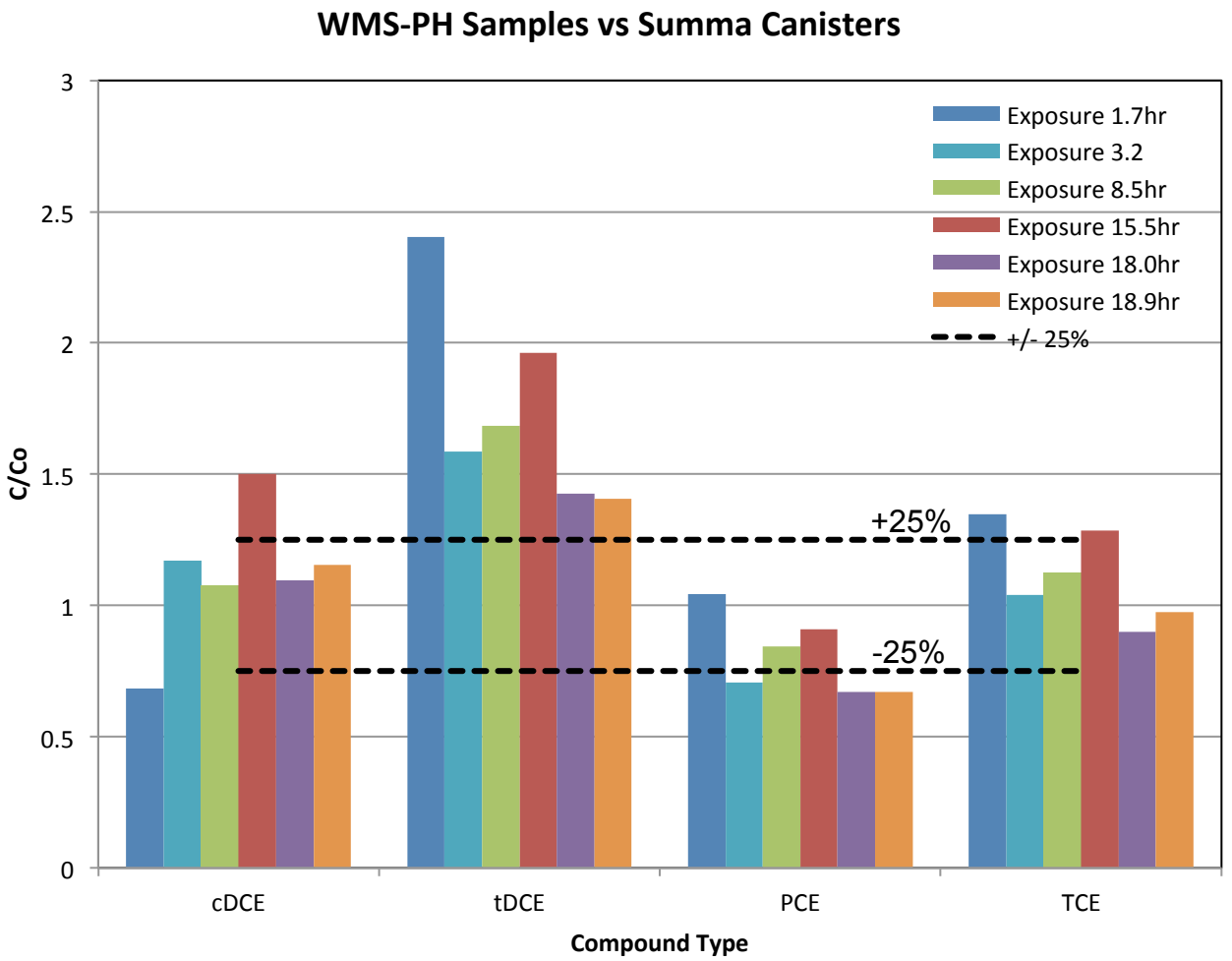




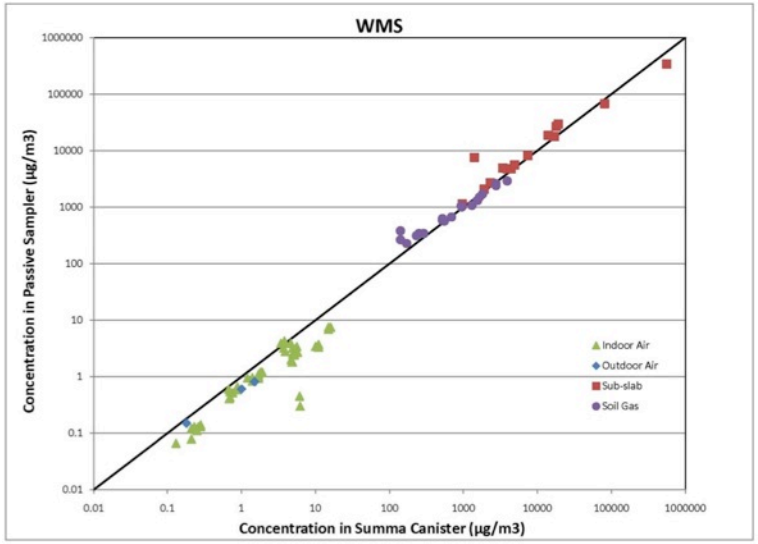
Limited to 1-inch diameter or less – Low-Uptake Rate Samplers

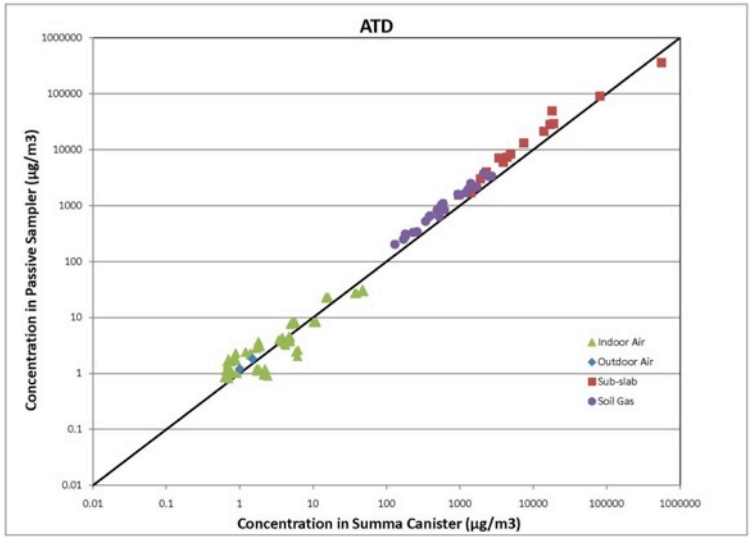
Temporary Passive - NAS JAX

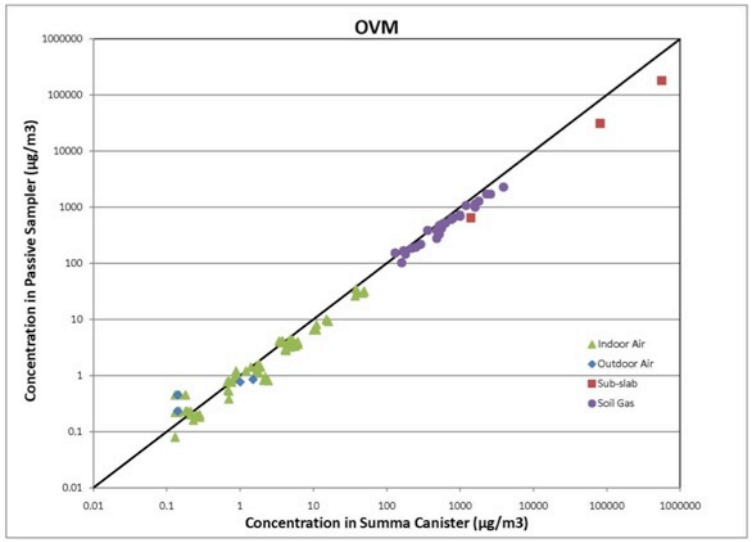


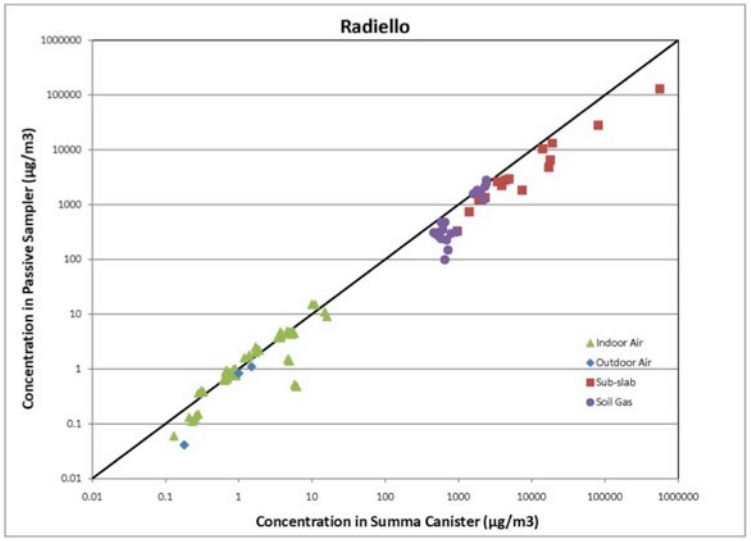


Overall Correlation between Passive and Active Samplers









Strong correlation to conventional samples over 6+ orders of magnitude

Quantitative results for soil vapor (a breakthrough)

Maybe we don’t need to be using so many Summa Canisters

Geosyntec consultants

Take-Home Messages

- Passive Sampling is becoming a reality for VI assessment
  - Strong positive correlation with Summa cans
  - Generally good consistency, but sensitive to wind, rain, temp.
- Minimize variability:
  - Integrate over time to manage temporal variability for indoor air
  - Simpler protocols for soil gas sampling – less operator error
- Benchmarking is recommended in the near-term
  - 1 of 10 samples collected with a duplicate by Summa/TO-15
  - Accounts for site-specific conditions, challenging compounds
- Study design takes a little more thought
  - Different samplers have different pros and cons
  - Sorbent selection is very important (just like TO-17)

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Questions/Comments?

tmcalary@geosyntec.com